Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 1 (2009) 875–880

Energy Procedia

www.elsevier.com/locate/procedia

GHGT-9

Developing strategies for the regeneration of polyethylenimine based CO_2 adsorbents

T.C. Drage[a]*, K.M. Smith[a], A. Arenillas[b] and C.E. Snape[a]

[a]*School of Chemical, Environmental and Mining Engineering, University of Nottingham, NG7 2RD, UK.*
[b]*Institudo Nacional del Carbon,CSIC, Apartado 73, 33080 Oviedo, Spain*

Abstract

Adsorption is considered to be one of the more promising technologies for capturing CO_2 from flue gases. The efficient adsorption of CO_2 at low partial pressures, associated with post-combustion capture, require chemical type adsorbents containing basic amine functional groups. It has been demonstrated that amine polymers, for example polyethylenimine (PEI), immobilised on various porous substrates, silica, zeolites and fly ash, are effective adsorbents for CO_2. When considering the use of adsorption for large scale CO_2 capture, the ease of regeneration and the lifetime of the adsorbents are critical factors in determining their efficiency, cost and therefore feasibility for use. In this paper two approaches, thermal swing adsorption (TSA) cycles over a range of temperatures and time in an atmosphere of CO_2 and thermally assisted pressure swing desorption, are explored for the regeneration of the PEI based adsorbents. The reactions occurring during the TSA regeneration of PEI based adsorbents in an atmosphere of CO_2, especially the formation of a thermostable complex between PEI and CO_2 above 130 °C are described. Identification of the complex by FTIR, XPS and ^{13}C NMR as a urea linkage will be described. Overall, the results from this research have implications for the selection of regeneration strategies of all amine based CO_2 adsorbents.

Keywords: Adsorption; CO_2 capture; Gas clean-up.

* Corresponding author. Tel.: +44 (0)115 951 4099 ; fax: +44 (0)115 951 4115.
E-mail address: trevor.drage@nottingham.ac.uk.

doi:10.1016/j.egypro.2009.01.116

1. Introduction

Increasing awareness of the influence of greenhouse gases on global climate has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO_2) emissions. Consequently, CO_2 capture and storage (CCS) from large point sources has recently received attention as a potential means of mitigating fossil fuel CO_2 emissions, with adsorption considered to be one of the most promising technologies. The success of such an approach is however dependent on the development of an adsorbent that, at flue gas temperatures, has both a high CO_2 selectivity and adsorption capacity and whilst under regeneration is stable, does not incur a significant energy penalty and therefore economic cost.

Some of the most successful adsorbents for the capture of CO_2 at close to atmospheric pressure have been developed via the alteration of the surface chemistry of porous substrates by impregnation with amine polymers [1-3]. Polyethylenimine (PEI) impregnated onto various substrates, low cost fly ash derived carbons [4] and MCM-41 [5] has produced highly effective CO_2 adsorbents.

The ease of regeneration and the lifetime of adsorbents are critical factors in determining their efficiency and therefore feasibility for use as CO_2 capture technologies. Previously two approaches, thermal swing (TSA) and pressure swing (PSA) regeneration have been described for PEI based adsorbents [6]. This paper describes the reactions occurring during the TSA regeneration of PEI based adsorbents in an atmosphere of CO_2. The influence to selected lifetime of the adsorbent, especially where the formation of a thermostable complex between PEI and CO_2 occurs above 130 °C during TSA cycles will be described. Overall, an understanding of this reaction will be crucial for the selection of regeneration cycles and the lifetime of amine based adsorbents.

2. Experimental

A proprietary inorganic support was used for the preparation of the adsorbent in this study. The inorganic support had a BET surface area of approximately 250 $m^2\ g^{-1}$, pore volumes of 1.7 cc g^{-1} and a mean pore diameter of approximately 20 nm. PEI, branched 1800 molecular mass form was supplied by Sigma-Aldrich, UK. The adsorbent was synthesised by the impregnation of a mesoporous inorganic supports with PEI. PEI was incorporated into the support by a wet impregnation method [5] and has been described elsewhere [6].

The stability of PEI in air, nitrogen and CO_2 over a temperature range of 25 - 200 °C was determined using a Perkin Elmer, Pyris 1, thermogravimetric analyser (TGA). Approximately 10 mg of adsorbent was placed in an alumina crucible and heated to 100 °C in a N_2 atmosphere at a flow rate of 20 ml min^{-1} and held isothermally for 30 minutes to remove any moisture. The temperature was decreased to 25 °C and the gas switched to either nitrogen, air or CO_2 with a flow rate of 20 ml min^{-1}, these conditions were maintained for 2 hours. The temperature was then increased gradually at a rate of 0.25 °C min^{-1}, the slow heating rate allowing equilibrium to be attained, up to 200 °C, with the weight change of the adsorbent monitored throughout.

High temperature adsorbent regeneration was performed by TGA. Following drying (100 °C in nitrogen for 30 minutes), the adsorption capacity was determined isothermally at 75 °C in a stream of CO_2 (20ml min^{-1}). Regeneration was undertaken by heating the adsorbent to 240 - 250 °C, at 15 °C min^{-1} for various periods of time from 1 min to 1 hour in nitrogen. This was followed by further determination of the CO_2 adsorption capacity after cooling the furnace to 75 °C at 15 °C min^{-1}.

Analysis of the adsorbent using solid start ^{13}C NMR, XPS, elemental analysis and DRIFT was performed as described in details elsewhere [6].

3. Results and Discussion

3.1. Polyethylenimine thermal stability

The thermal stability of the supported PEI in nitrogen, air and CO_2 up to 200 °C is presented in Figure 1. In an atmosphere of air and nitrogen the mass of adsorbent decreases between 95 and 125 °C, most likely as a result of moisture loss, either adsorbed or tightly bound in the inorganic support. It is also possible that slow volatilization of PEI may also be occurring at these temperatures. Above 135 °C a more rapid decrease in mass occurs, especially in

the presence of air where the weight decrease is as a result of volatilization and / or thermal degradation. In the presence of CO_2 there is a significant increase in mass as a result of adsorption of carbon dioxide which is constant up to approximately 85 °C, above this temperature CO_2 adsorption becomes less favourable and adsorption capacity decreases to a minima at 135 °C. Whilst it would be expected that the adsorbent would undergo a further weight loss as seen in N_2 and air above 135 °C, an increase in weight is observed. This indicates that a further reaction is taking place between the amine and CO_2 resulting in the formation of a thermostable complex. The composition of this complex, which is further evident from a colour change in the adsorbent, will be explored further by post-test analysis.

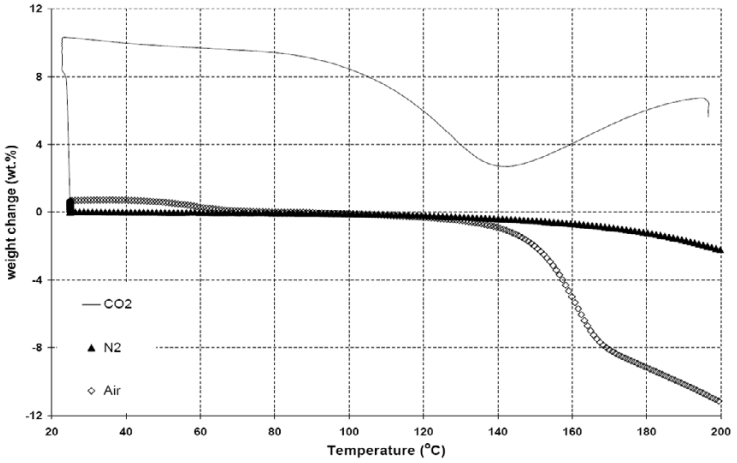

Figure 1. TGA profile for the behaviour of the PEI based adsorbent in N_2, CO_2 and air, whilst slowly heated from 25 - 200 °C at 0.25 °C min^{-1} [6].

3.2. Thermal swing adsorption cycles

Thermal swing regeneration in an atmosphere of CO_2 is an attractive method for the regeneration of the adsorbent. The use of CO_2 as sweep gas will result in the generation of a pure stream of the gas without the need for further gas separations. The influence of temperature on the cyclic sorption capacity is presented in Fig. 2. Cyclic adsorption capacity is measured as a percentage during the first adsorption cycle therefore, 100% corresponds to adsorption of 2.4 mmol g^{-1} of CO_2. It is evident that increasing the regeneration temperature from 110 to 145 °C results in a steady increase in cyclic adsorption capacity. Including and above 145 °C approximately 90% of the original sorption capacity is recovered, giving a cyclic capacity of 2.1 mmol g^{-1}.

The formation of the thermostable complex is crucial factor for the regeneration of the adsorbents. Regeneration temperatures above 145 °C whilst recovering approximately 90% of the original adsorption capacity, results in significant decrease from the first to the second regeneration cycle, leading to a 10 % loss in capacity between the two cycles at 180 °C. This destructive effect of the thermostable complex on adsorption capacity can be further illustrated by simulating a greater number of regeneration cycles, at 130 - 140 °C resulting in a decrease of approximately 80 % in adsorption capacity after approximately 1000 regeneration cycles (Figure 3).

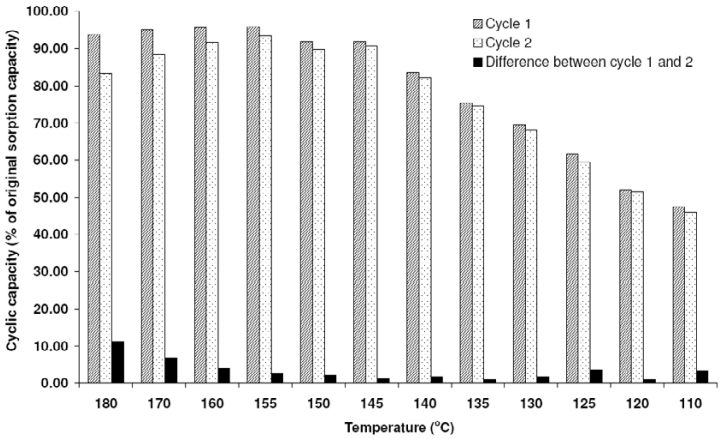

Figure 2 – Effect of regeneration temperature over successive regeneration cycles [6]

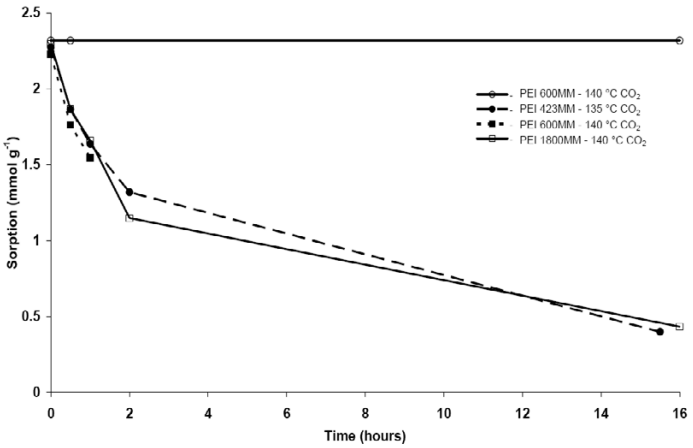

Figure 3. Influence of numerous regeneration cycles on PEI adsorption capacity [6].

3.3. PEI CO_2 reactions

The reaction between CO_2 and polyethylenimine (PEI) is proposed to occur by the formation of a carbamate ion [7] and is similar to the absorption of CO_2 with primary alkanolamines [8]. The reaction is proposed to be a two stage reaction, similar to that of CO_2 absorption with amine solvents, with two moles of amine reacting with one mole of CO_2 by a zwitterion mechanism, followed by base catalysed deprotonation via a second amine group [9] to form a stable carbamate ion. The reaction is reversible, allowing for the adsorbent to be regenerated by thermal, vacuum or pressure swing adsorption cycles.

$$CO_2 + 2R_2NH \leftrightarrow R_2NH_2^+ + R_2NCOO^- \quad <1>$$

$$CO_2 + 2R_3N \leftrightarrow R_4N^+ + R_2NCOO^- \quad <2>$$

Analysis has been performed to determine the composition of the product formed after 16 hours in CO_2 at 140 °C to generate a material almost completely composed of the thermostable complex (Figure 3). As the resultant

complex was insoluble in organic solvents, analysis was required in the solid state. Complete analysis of the reaction [6] revealed the reaction between CO_2 and PEI above 130 °C to result in the formation of a urea linkage between two amine groups and the loss of water. Whether the reaction occurs from secondary reaction of the carbamate ion formed on adsorption of CO_2 (Reaction <3>) or direct reaction of CO_2 and the amine groups of PEI (Reaction <4>) cannot be determined from the results of this study (where R can be either H or another PEI monomer).

$$R_2NH_2^+ + R_2NCOO^- \leftrightarrow R_2NCONR_2 + H_2O \quad <3>$$

$$2R_2NH + CO_2 \leftrightarrow R_2NCONR_2 + H_2O \quad <4>$$

What is clearly evident from the results presented (Fig. 3) is that the rate of formation of the urea linkage occurs at a slower rate than the formation of the reversible carbamate ions (Reactions <1> and <2>). The formation of dialkyl urea and possible reaction mechanisms has previously been reported from the direct reaction of amines and CO_2 by a number of routes [9]. Regeneration using nitrogen as a stripping gas

3.4. Regeneration using inert stripping gas

To avoid the problems associated with TSA cycles in CO_2, pressure swing adsorption (TPSA) has been explored using nitrogen as a simulated stripping gas, to lower the partial pressure of CO_2 [6]. Desorption profiles using N2 as a stripping gas for the adsorbent loaded with 40 wt.% PEI are presented for a range of temperatures and flow rates, 50 ml min^{-1} and 100 ml min^{-1} (Fig. 4). Desorption temperature results in an increased rate of CO_2 desorption (Fig. 6). Regeneration of the adsorbents at 75 °C is a lengthy process requiring a large ratio of N_2 to CO_2. The benefit of increased regeneration temperature is demonstrated by the dramatic reduction in the amount of nitrogen required to desorb the CO_2 approximately 50% when regeneration temperature is increased from 120–140 °C [6]. It is also evident that complete regeneration of the adsorbent is a lengthy process, with 100% compared to 99% of adsorbed CO_2 removal requiring, for example a five fold increase on the moles of nitrogen stripping gas at 140 °C and 50 ml min^{-1} [6]. The best conditions for regeneration of the PEI based adsorbent required approximately five times as much N_2 to desorb 90% of the adsorbed CO_2 (mol/mol) at 140 °C. Although nitrogen would not be used to regenerate adsorbents, the efficiency of the pressure swing method induced by using nitrogen as a stripping gas suggests that steam stripping is a viable technique for regeneration. Especially as the technique potentially overcomes the problems identified for the thermal regeneration of the adsorbents in a CO_2 atmosphere. Using water vapour as a stripping gas is an ideal technique in that the two gases can easily be separated by condensation of the water phase. Future work will simulate steam stripping as a technique for the regeneration of PEI based adsorbents.

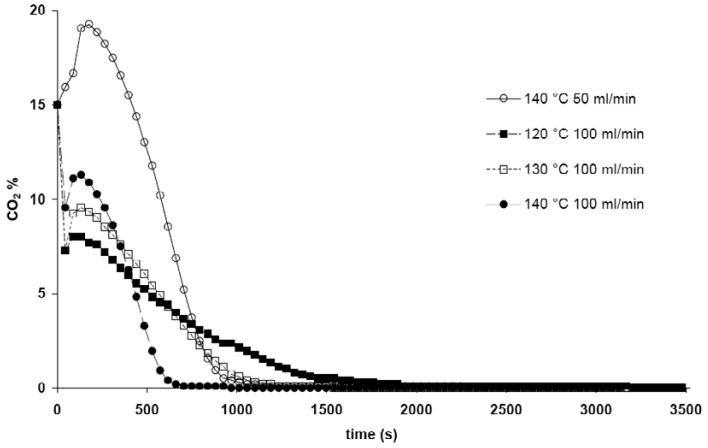

Figure 4. Thermal pressure swing desorption profiles [6].

4. Conclusions

Study of the cyclic performance of a PEI based adsorbent using thermal swing regeneration in an atmosphere of CO2, whilst resulting in efficient cycling of the adsorbent, resulted in successive loss of adsorption capacity over numerous regeneration cycles. The loss of adsorption capacity was attributed to the bonding of CO2 into the PEI polymer be the formation of a urea type linkage above 135 °C.

The use of nitrogen stripping gas at elevated temperatures (e.g. 140 °C) has been used to demonstrate to regenerate the adsorbent using small quantities of stripping gas. Although nitrogen was used as a stripping gas in this example, and would not be used in real application of the technology, the results demonstrate that there is potential for the use of steam stripping as a means of regeneration. Further research is required to determine the cyclic adsorption capacities of PEI based adsorbents.

Whilst this work has involved exclusively the regeneration of PEI based adsorbent, it is probable that similar reaction will occur above 120 °C for other amine based adsorbent materials. Therefore regeneration strategies will need to be carefully selected to avoid the irreversible degradation of adsorption performance as a result of urea linkage formation.

5. Acknowledgements

The authors thank The Carbon Trust, for financial support. TD would like to thank the EPSRC (Advanced Research Fellowship EP/C543201/1) for funding.

6. References

1. P.J. Birbara, T.P. Filburn, T.A. Nalette, U.S. Patent No 5,876,488 (1999)
2. T. Filburn, R. A. Weiss, J. Helbe, S. Huang and W. Papale. (2002). Fuel Chemistry Division Preprints 47 (2002), 61.
3. O. Leal, C. Bolivar, C. Ovales, J.J. Garcia, Y. Espidel. (1995) Inorganica Chimica Acta 240 (1995) 183.
4. A. Arenillas, K.M. Smith, T.C. Drage, C.E. Snape. Fuel, 84 (2005) 2204.
5. X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni. Microporous and Mesoporous Materials, 62 (2003) 29.
6. T.C. Drage, A. Arenillas, K.M. Smith, and C.E. Snape. Microporous and Mesoporous Materials. (2008), doi:10.1016/j.micromeso.2008.05.009
7. K. Otsubo, T. Tanemura, K. Nitta, M. Oguchi, N. Nakabayashi, S. Kimura, H. Kuroda, International symposium on space technology and science, Japan, (1992) 1431.
8. R. Carey, A. Gomezplata, A. Sarich. Ocean Engineering 10 (1983) 227.
9. J. Fournier, Journal of Organic Chemistry 56 (1991) 4456.